

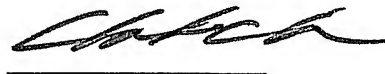
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For and on behalf of RWS Group Ltd  
The 30th day of October 2007

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**Priority Certificate  
for the filing of a Patent Application**

**File Reference:** 102 61 804.6

**Filing date:** 19 December 2002

**Applicant/Proprietor:** Argolinz Melamin GmbH, Linz/AT

**Title:** Direct synthesis process for preparing etherified melamine resin condensates, melamine resin condensates and their use

**IPC:** C 08 G, C 08 J, C 08 L

**The attached documents are a correct and accurate reproduction of the original submission for this Application.**

Munich, 12 December 2003

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Description

Direct synthesis process for preparing etherified  
melamine resin condensates, melamine resin condensates  
5 and their use

The invention relates to a direct synthesis process for  
etherified melamine resin condensates according to the  
precharacterizing clause of Claim 1, to a use of the  
10 melamine resin condensates according to Claim 21 and to  
melamine resin condensates according to Claim 22.

Direct synthesis processes for preparing etherified  
melamine resin condensates are known.

15 According to DE-A 25 16 349 and US-A 4,425,466,  
etherified methylolaminotriazines can be prepared by  
reacting aminotriazines with formaldehyde and alcohols  
in the presence of strong organic acids at from 80 to  
20 130°C. BE-A 623 888 describes the use of ion exchangers  
in the direct preparation of etherified formaldehyde  
resins. The disadvantage with these known processes is  
that they cannot prepare relatively highly condensed  
melamine resin ethers, and that the melamine resin  
25 ethers formed still contain hydroxymethyleneamino  
groups bonded to the triazine rings of the melamine  
resin condensates and still retain -NH-CH<sub>2</sub>-O-CH<sub>2</sub>-NH-  
groups linking the triazine rings, the result of this  
being that, during curing, formaldehyde is eliminated  
30 and microcracks form in the cured resins and coatings.

It is an object of the invention to provide a direct  
synthesis process for preparing etherified melamine  
resin condensates which have average molecular weights  
35 of from 500 to 50 000 and which are free from hydroxy-  
methyleneamino groups bonded to the triazine rings

and from  $\text{-NH-CH}_2\text{-O-CH}_2\text{-NH-}$  groups linking the triazine rings.

5 This object is achieved by way of a direct synthesis process in which

a) in a first step of the reaction, an etherified melamine resin precondensate is prepared in alcoholic solution,

10 b) in at least one vaporization step, the concentration of the etherified melamine resin precondensate in alcoholic solution is increased,  $\text{C}_4\text{-C}_{18}$  alcohols, diols of the type represented by  $\text{HO-R-OH}$  and/or tetrahydric alcohols based on erythritol being added to the melamine resin precondensate prior to, during and/or after the  
15 concentration-increase process,

c) in a second step of the reaction, the increased-concentration melamine resin precondensate is reacted, using a mixer, in particular a kneader.

20 In one advantageous embodiment of the inventive process, after the second step of the reaction the etherified melamine resin condensate is discharged and pelletized.

Methanol is advantageously used as alcohol in the first  
25 step of the reaction. There are two advantageous methods for carrying out the methylation and the etherification.

On the one hand, the methylation and the etherification  
30 are executed in succession, and on the other hand the methylation and the etherification are executed simultaneously.

In the first method, by way of example, the melamine is  
35 first methylolated at a preferred pH of from about 7 to 9 by adding a formaldehyde component, such as formaldehyde or a mixture of formaldehyde and methanol,

and the resultant methylolmelamine is then etherified under acidic conditions, using an alcohol, preferably methanol. This etherification preferably takes place at temperatures of from 70 to 160°C, at pressures from 1.3 to 20 bar and at a preferred pH of from 5.5 to 6.5. The reaction time may be varied from a few seconds to 1 hour and is typically from 5 to 40 minutes. Continuous and/or batchwise operation is possible here.

10 The second method consists in simultaneous methylolation and etherification in the first step of the reaction. By way of example, methanol is the alcohol used for the etherification. By way of example, the dispersion comprising from 10 to 60% by weight of  
15 melamine is prepared by introducing melamine into methanol or a mixture of from 5 to 95% by weight of methanol and from 95 to 5% by weight of C<sub>4</sub>-C<sub>8</sub> hydrocarbons at a temperature of from 30 to 95°C. Once a pH of from 5.5 to 6.5 has been established, an  
20 aqueous formaldehyde solution with a formaldehyde concentration of from 35 to 55% by weight and/or p-formaldehyde is metered in as formaldehyde component. The formaldehyde solution may comprise up to 15% by weight of methanol. The reaction mixture is reacted at  
25 a reaction temperature of from 70 to 110°C, at a pressure of from 1.3 to 5 bar and for a reaction time of from 5 to 40 minutes to give etherified melamine precondensates. The resultant alcoholic solution of the etherified melamine resin precondensate is cooled to 40  
30 - 60°C.

The molar melamine/formaldehyde ratio is advantageously from 1:2 to 1:4. The molar melamine/methanol ratio is advantageously from 1:10 to 1:20. These molar ratios  
35 apply to both methods for carrying out the first step of the reaction.

Particularly suitable C<sub>4</sub>-C<sub>8</sub> hydrocarbons for dispersing melamine in mixtures of from 5 to 95% by weight of methanol and from 95 to 5% by weight of C<sub>4</sub>-C<sub>8</sub> hydrocarbons in the first step of the reaction are:  
5 isobutane, pentane, heptane and/or isooctane.

In the first step of the reaction in one embodiment of the inventive process, the formaldehyde component used comprises a mixture of 35% by weight of formaldehyde,  
10 15% by weight of methanol and 50% by weight of water. Alternatively, a mixture of 50% by weight of formaldehyde and 50% by weight of water may be used in the first step of the reaction.

15 Paraformaldehyde may also be used as formaldehyde component in the first step of the reaction.

The preferred reaction temperature in the first step of the reaction is in the range from 70 to 160°C,  
20 particularly preferably from 95 to 100°C.

In one preferred embodiment of the first step of the reaction, the reaction takes place in the presence of acidic, or of a mixture of acidic and basic, ion  
25 exchangers. By way of example, suitable ion exchangers are ion exchangers based on chloromethylated and trimethylolamine-aminated styrene-divinylbenzene copolymers or based on sulphonated styrene-divinylbenzene copolymers.

30 The concentration of the alcoholic, preferably methanolic, melamine resin precondensate solution obtained in the first step of the reaction is then increased through at least one vaporization step.

35 It is preferable to carry out two vaporization steps. By way of example, once a pH of less than 10 has been established,

the concentration of the etherified melamine resin precondensate is increased in a first evaporator stage for removal of the water/methanol mixture at temperatures of from 60 to 100°C and at a pressure of  
5 from 0.2 to 1 bar, until the solids content of etherified melamine resin precondensate is from 65 to 85% by weight, and is increased in a second evaporator stage intended to achieve a solids content of etherified melamine resin precondensate of from 95 to  
10 99% by weight at from 60 to 120°C and from 0.1 to 1 bar.

Prior to and/or during the concentration increase process, i.e. prior to the first and/or prior to the  
15 second evaporator stage and/or after the concentration-increase process, i.e. prior to the second step of the reaction, C<sub>4</sub>-C<sub>18</sub> alcohols, diols of the type represented by HO-R-OH and/or tetrahydric alcohols based on erythritol may be added to the melamine resin  
20 precondensate. The molecular weights of these diols are preferably from 62 to 20 000.

Prior to and/or during the concentration increase-process, i.e. prior to the first and/or prior to the  
25 second vaporization stage and/or after the concentration-increase process, i.e. prior to the second step of the reaction, anhydrides and/or acids dissolved in alcohols or in water may be added to the melamine resin precondensate.

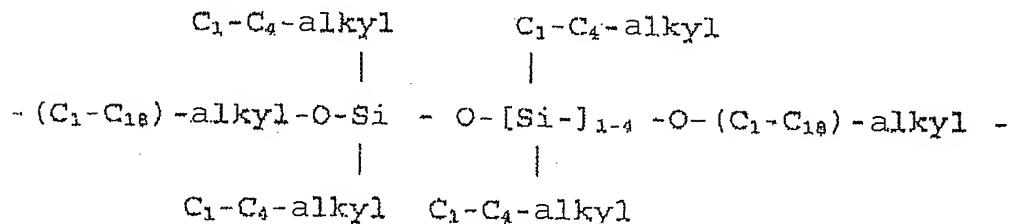
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The ratio of the ether groups of the melamine precondensate to the hydroxy groups of the added C<sub>4</sub>-C<sub>18</sub> alcohols and/or diols may be from 1:0.5 to 1:0.1, for example. Examples of suitable C<sub>4</sub>-C<sub>18</sub> alcohols are  
35 butanol, ethylhexyl alcohol, dodecyl alcohol and stearyl alcohol.

The added diols are preferably diols where the substituent R has one of the following structures:

- 5  $C_2-C_{18}$ -alkylene,  
 $-CH(CH_3)-CH_2-O-(C_2-C_{12})$ -alkylene- $O-CH_2-CH(CH_3)-$ ,  
 $-CH(CH_3)-CH_2-O-(C_2-C_{12})$ -arylene- $O-CH_2-CH(CH_3)-$ ,  
 $-(CH_2-CH_2-CH_2-CH_2-CO-)_x-(CH_2-CHR)_y-$   
 $-[CH_2-CH_2-O-CH_2-CH_2]_n-$ ,  
 $-[CH_2-CH(CH_3)-O-CH_2-CH(CH_3)]_n-$ ,  
 $-[-O-CH_2-CH_2-CH_2-CH_2-]_n-$ ,  
10  $-[(CH_2)_{2-8}-O-CO-(C_6-C_{14})$ -arylene- $CO-O-(CH_2)_{2-8}]_n-$ ,  
 $-[(CH_2)_{2-8}-O-CO-(C_2-C_{12})$ -alkylene- $CO-O-(CH_2)_{2-8}]_n-$ ,  
where  $n = 1 - 200$ ;

15 sequences which contain siloxane groups and are represented by the type

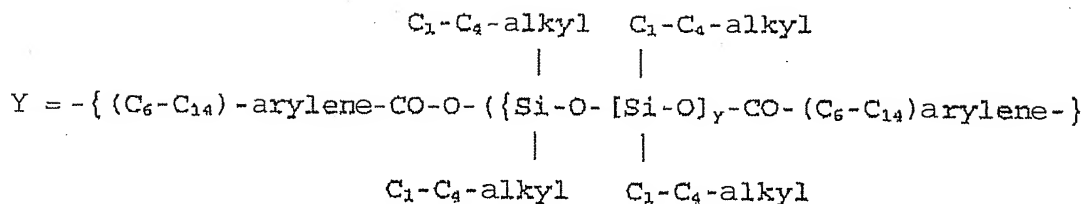


polyester sequences which contain siloxane groups and are represented by the type

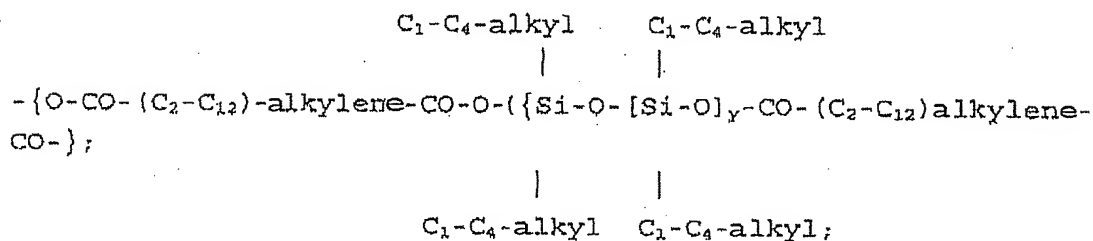
20  $-[(X)_r-O-CO-(Y)_s-CO-O-(X)_r]-$ ,  
where

$X = \{(CH_2)_{2-8}-O-CO-(C_6-C_{14})$ -arylene- $CO-O-(CH_2)_{2-8}-\}$   
or  
 $-\{(CH_2)_{2-8}-O-CO-(C_2-C_{12})$ -alkylene- $CO-O-(CH_2)_{2-8}-\};$





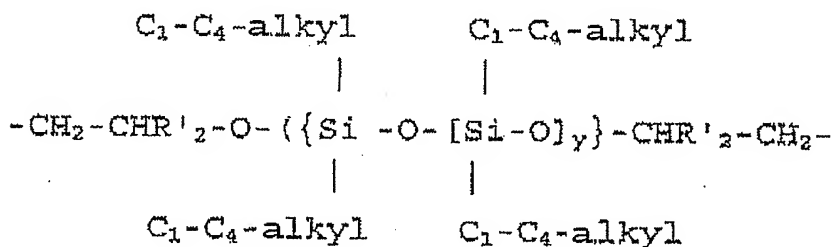
or



where  $r = 1 - 70$ ;  $s = 1 - 70$  and  $y = 3 - 50$ ;

5

polyether sequences which contain siloxane groups and are represented by the type



where  $\text{R}'_2 = \text{H}$ ;  $\text{C}_1\text{-C}_4\text{-alkyl}$  and  $y = 3 - 50$ ;

10

sequences based on alkylene oxide adducts of melamine and represented by the type of

2-amino-4,6-di-( $\text{C}_2\text{-C}_4$ )alkyleneamino-1,3,5-triazine sequences

15

phenol ether sequences based on dihydric phenols and on  $\text{C}_2\text{-C}_8$  diols and represented by the type of

-( $\text{C}_2\text{-C}_8$ )alkylene-O-( $\text{C}_6\text{-C}_{18}$ )-arylene-O-( $\text{C}_2\text{-C}_8$ )-alkylene sequences.

Examples of diols of the type represented by  $\text{HO-R}_1\text{-OH}$ , where  $\text{R}_1 = \text{C}_2\text{-C}_{18}\text{-alkyl}$ , are ethylene glycol, butanediol, octanediol, dodecanediol and octadecanediol.

- 5 Examples of diols of the type represented by  $\text{HO-R}_2\text{-OH}$ , where  $\text{R}_2 = -[\text{CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2]_n-$  and  $n = 1\text{-}200$ , are polyethylene glycols with molecular weights of from 500 to 5 000.

Examples of diols represented by the type  $\text{HO-R}_3\text{-OH}$ , where

- 10  $\text{R}_3 = -[\text{CH}_2\text{-CH}(\text{CH}_3)\text{-O-CH}_2\text{-CH}(\text{CH}_3)]_n-$  and  $n = 1\text{-}200$ , are polypropylene glycols with molecular weights of from 500 to 5 000.

Examples of diols of the type represented by  $\text{HO-R}_4\text{-OH}$ , where

- 15  $\text{R}_4 = -[-\text{O-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-]_n-$  and  $n = 1\text{-}200$ , are polytetrahydrofurans with molecular weights of from 500 to 5 000.

Examples of diols of the type represented by  $\text{HO-R}_5\text{-OH}$ , where

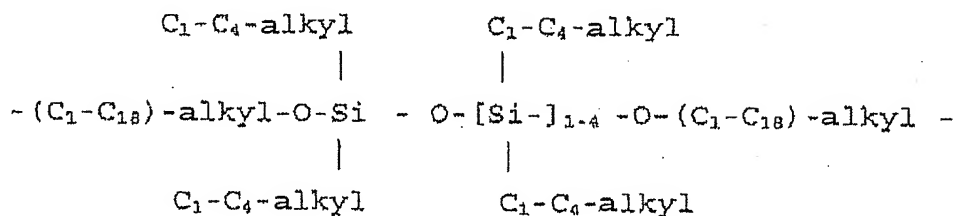
- 20  $\text{R}_5 = -[(\text{CH}_2)_{2-8}\text{-O-CO-(C}_6\text{-C}_{14}\text{)-arylene-CO-O-(CH}_2)_{2-8}]_n-$  and  $n = 1\text{-}200$ , are esters and polyesters based on saturated dicarboxylic acids, such as terephthalic acid, isophthalic acid or naphthalenedicarboxylic acid and on diols, such as ethylene glycol, butanediol, neopentyl glycol and/or  
25 hexanediol. Preference is given to bis(hydroxyethyl) terephthalate as ester.

Examples of diols of the type represented by  $\text{HO-R}_6\text{-OH}$ , where

- 30  $\text{R}_6 = -[(\text{CH}_2)_{2-8}\text{-O-CO-(C}_2\text{-C}_{12}\text{)-alkylene-CO-O-(CH}_2)_{2-8}]_n$  and  $n = 1\text{-}200$ , are polyesters based on saturated dicarboxylic acids, such as adipic acid and/or succinic acid, on unsaturated dicarboxylic acids, such as maleic acid, fumaric acid and/or itaconic acid, and on diols, such as  
35 ethylene glycol, butanediol, neopentyl glycol and/or hexanediol.

Examples of diols of the type represented by HO-R<sub>7</sub>-OH, where

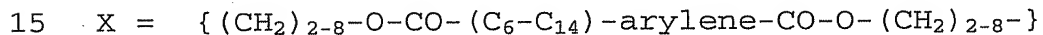
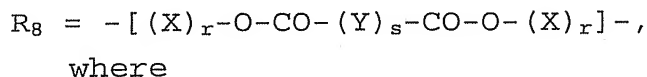
R<sub>7</sub> = sequences containing siloxane groups and represented by the type



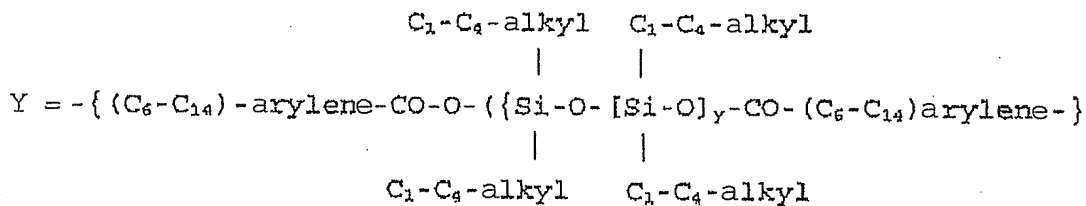
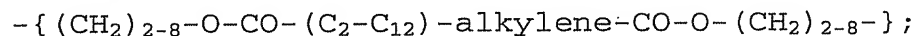
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are 1,3-bis(hydroxybutyl)tetramethyldisiloxane and 1,3-bis(hydroxyoctyl)tetraethyldisiloxane.

Examples of polyester sequences having diols containing  
10 siloxane groups and represented by the type HO-R<sub>8</sub>-OH, where

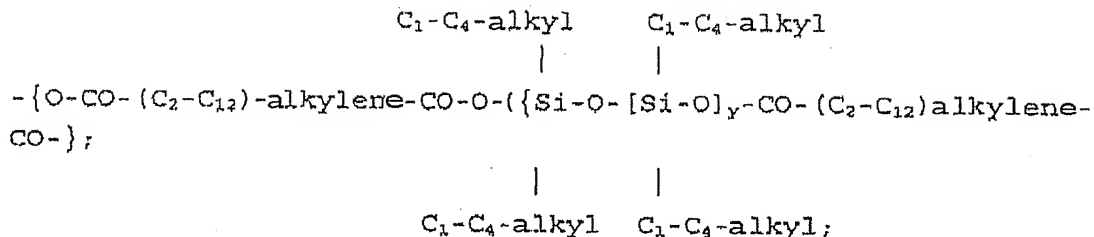


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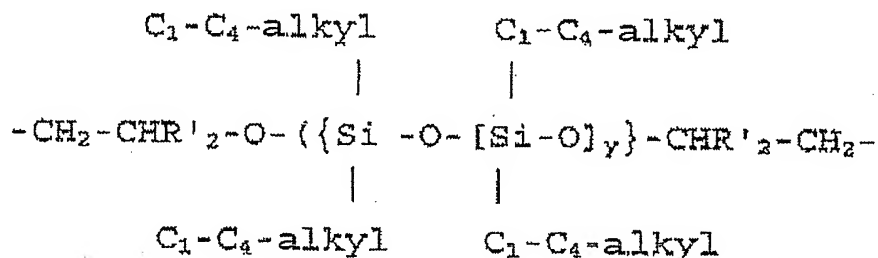
or

20



where  $r = 1 - 70$ ;  $s = 1 - 70$  and  $y = 3 - 50$ ,  
are polyesters containing hydroxy end groups and based  
on aromatic  $\text{C}_6\text{-C}_{14}$ -arylenedicarboxylic acids, such as  
5 terephthalic acid or naphthalenedicarboxylic acid, or  
on aliphatic  $\text{C}_2\text{-C}_{12}$ -alkylenedicarboxylic acids, such as  
adipic acid, maleic acid or pimelic acid. Diols, such  
as ethylene glycol, butanediol, neopentyl glycol or  
hexanediol, and on siloxanes, such as hexamethyl-  
10 disiloxane or  $\alpha,\omega$ -dihydroxypolydimethylsiloxane.

Examples of polyetherdiols  $\text{HO-R}_9\text{-OH}$  containing siloxane  
groups, where  $\text{R}_9$  is polyether sequences represented by  
the type



15

where  $\text{R}'_2 = \text{H}$ ;  $\text{C}_1\text{-C}_4\text{-alkyl}$  and  $y =$  from 3 to 50 are  
polyetherdiols based on siloxanes, such as hexamethyl-  
disiloxane or  $\alpha,\omega$ -dihydroxypolydimethylsiloxane, and on  
alkylene oxides, such as ethylene oxide or propylene  
20 oxide.

Examples of diols based on alkylene oxide adducts of  
the melamine represented by the type

25 2-amino-4,6-bis(hydroxy-( $\text{C}_2\text{-C}_4$ )-alkyleneamino)-1,3,5-  
triazine

are diols based on melamine and ethylene oxide or propylene oxide.

5 Examples of phenol ether diols based on dihydric phenols and C<sub>2</sub>-C<sub>8</sub> diols represented by the type

bis(hydroxy-(C<sub>2</sub>-C<sub>8</sub>)-alkylene-O-)(C<sub>6</sub>-C<sub>18</sub>)-arylene are ethylene oxide adducts or propylene oxide adducts onto diphenylolpropane.

10

Besides diols as polyhydric alcohols, trihydric alcohols, such as glycerol, or tetrahydric alcohols based on erythritol, or mixtures of these with dihydric alcohols, may also be used in the direct synthesis  
15 process.

If C<sub>4</sub>-C<sub>18</sub> alcohols and/or diols of the type represented by HO-R-OH are added prior to the first evaporator stage and/or prior to the second evaporator stage,  
20 mixing sections are installed to homogenize the components prior to the evaporator stages.

In a second step of the reaction, the melamine resin precondensate treated with alcohols and/or with diols  
25 is reacted in a kneader. This is preferably a continuous kneader. The reaction time in the kneader is from about 2 to 12 min, and the reaction temperature is from about 180 to 250°C. Unreacted reactants are removed during venting in the kneader, and the  
30 etherified melamine resin condensate is then preferably discharged and granulated.

Up to 75% by weight of fillers and/or reinforcing fibres, other reactive polymers of the type represented  
35 by ethylene copolymers, maleic anhydride copolymers,

modified maleic anhydride copolymers, poly(meth)acrylates, polyamides, polyesters and/or polyurethanes may also be added to the kneader, as well as up to 2% by weight of stabilizers, UV absorbers and/or auxiliaries, each weight  
5 being based on the etherified melamine resin condensates.

The continuous kneaders in the second step of the reaction may comprise twin-screw extruders which have vent zones after the feed zone and also after the reaction zone.  
10 These twin-screw extruders may have an L/D ratio of from 32 to 48 with a corotating arrangement of screws.

In principle, the kneaders used may also comprise other, at least to some extent self-cleaning, continuously  
15 operating machines suitable for the processing of highly viscous substances and having vacuum venting (e.g. Buss Co-Kneader, single-screw extruders, extruders in a cascade arrangement, single- or twin-screw kneaders of the type represented by LIST ORP; CRP, Discotherm, etc.).

20 To remove any inhomogeneity, the melt may be conveyed into a melt filter, using a gear pump. The melt may be converted into pellets in pelletizers or in pastille-production systems by metering the melt through a feed  
25 device onto a continuous steel belt and cooling and solidifying the pastilles deposited.

Examples of suitable fillers which may be metered into the continuous kneader during the direct synthesis process  
30 are:  $\text{Al}_2\text{O}_3$ ,  $\text{Al}(\text{OH})_3$ , barium sulphate, calcium carbonate, glass beads, siliceous earth, mica, powdered quartz, powdered slate, hollow microbeads, carbon black, talc, powdered stone, wood flour, cellulose powder and/or ground shells or ground kernels, e.g. ground peanut shells or  
35 ground olive kernels. Preferred fillers are phyllosilicates of the type represented by montmorillonite,

bentonite, kaolinite, muscovite, hectorite, fluorohectorite, kanemite, revdite, grumantite, ilerite, saponite, beidelite, nontronite, stevensite, laponite, taneolite, vermiculite, halloysite, volkonskoite, magadite, rectorite,  
5 kenyaite, sauconite, borofluorophlogopites and/or synthetic smectites.

Examples of suitable reinforcing fibres which may be metered into the continuous kneader during the direct synthesis process are inorganic fibres, in particular glass  
10 fibres and/or carbon fibres, natural fibres, in particular cellulose fibres, such as flax, jute, kenaf, and wood fibres, and/or synthetic fibres, in particular fibres of polyacrylonitrile, of polyvinyl alcohol, of polyvinyl acetate, of polypropylene, of polyesters and/or of  
15 polyamides.

Examples of reactive polymers of the type represented by ethylene copolymers, which can be metered into the continuous kneader during the direct synthesis process are partially hydrolyzed ethylene-vinyl acetate copolymers,  
20 ethylene-butyl acryl-acrylic acid copolymers, ethylene-hydroxyethyl acrylate copolymers and ethylene-butyl acrylate-glycidyl methacrylate copolymers.

Examples of reactive polymers of the type represented by maleic anhydride copolymers which may be metered into the continuous kneader during the direct synthesis process are  
25 C<sub>2</sub>-C<sub>20</sub> olefin-maleic anhydride copolymers and copolymers of maleic anhydride and C<sub>8</sub>-C<sub>20</sub> vinylaromatics.

Examples of the C<sub>2</sub>-C<sub>20</sub> olefin components which may be present in the maleic anhydride copolymers are ethylene,  
30 propylene, 1-butene, isobutene, diisobutene, 1-hexene, 1-octene, 1-heptene, 1-pentene, 3-methyl-1-butene, 4-methyl-1-pentene, methylethyl-1-pentene, ethyl-1-pentene, ethyl-1-hexene, 1-octadecene and 5,6-dimethylnorbornene.

Examples of the C<sub>8</sub>-C<sub>20</sub> vinylaromatic components which may be  
35 present in the maleic anhydride copolymers are

styrene,  $\alpha$ -methylstyrene, dimethylstyrene, isopropenylstyrene, p-methylstyrene and vinylbiphenyl.

5 Examples of modified maleic anhydride copolymers which may be metered into the continuous kneader during the direct synthesis process are partially or completely esterified, amidated or, respectively, imidated maleic anhydride copolymers.

10 Particularly suitable substances are modified copolymers of maleic anhydride with  $C_2$ - $C_{20}$  olefins or with  $C_8$ - $C_{20}$  vinylaromatics with a molar ratio of from 1:1 to 1:9 and weight-average molecular weights of from 5 000 to 500 000, which have been reacted with ammonia,  
15 with  $C_1$ - $C_{18}$  monoalkylamines, with  $C_6$ - $C_{18}$  aromatic monoamines, with  $C_2$ - $C_{18}$  monoaminoalcohols, with monoaminated poly( $C_2$ - $C_4$ -alkylene) oxides of molecular weight from 400 to 3 000, and/or with monoetherified poly( $C_2$ - $C_4$ -alkylene) oxides of molecular weight from 100  
20 to 10 000, the molar ratio of anhydride groups in the copolymer to ammonia, amino groups of the  $C_1$ - $C_{18}$  monoalkylamines, of the  $C_6$ - $C_{18}$  aromatic monoamines or the  $C_2$ - $C_{18}$  monoaminoalcohols or monoaminated poly( $C_2$ - $C_4$ -alkylene) oxide and/or hydroxy groups poly( $C_2$ -  
25  $C_4$ -alkylene) oxide being from 1:1 to 20:1.

Examples of reactive polymers of the type represented by poly(meth)acrylates which can be metered into the continuous kneader during the direct synthesis process  
30 are copolymers based on functional unsaturated (meth)acrylate monomers, such as acrylic acid, hydroxyethyl acrylate, glycidyl acrylate, methacrylic acid, hydroxybutyl methacrylate or glycidyl methacrylate, and on non-functional unsaturated  
35 (meth)acrylate monomers, such as ethyl acrylate, butyl acrylate, ethylhexyl acrylate, methyl methacrylate ethyl acrylate and/or butyl methacrylate, and/or on  $C_8$ - $C_{20}$ -vinylaromatics. Preference is given to copolymers based on methacrylic acid, hydroxyethyl acrylate,



methvl methacrylate and styrene. Examples of reactive polymers of the type represented by polyamides which may be metered into the continuous kneader during the direct synthesis process are nylon-6, nylon-6,6, nylon-11, 5 nylon-12, polyaminoamides composed of polycarboxylic acids and of polyalkyleneamines, and also the corresponding methoxylated polyamides.

Examples of reactive polymers of the type represented by 10 polyesters which may be metered into the continuous kneader during the direct synthesis process are polyesters with molecular weights of from 2 000 to 15 000 composed of saturated dicarboxylic acids, such as phthalic acid, isophthalic acid, adipic acid and/or 15 succinic acid, of unsaturated dicarboxylic acids, such as maleic acid, fumaric acid and/or itaconic acid, and of diols, such as ethylene glycol, butanediol, neopentyl glycol and/or hexanediol. Preference is given to branched polyesters based on neopentyl glycol, 20 trimethylolpropane, isophthalic acid and azelaic acid.

Examples of reactive polymers of the type represented by polyurethanes which may be metered into the continuous kneader during the direct synthesis process are non- 25 crosslinked polyurethanes based on tolylene diisocyanate, diphenylmethane diisocyanate, butane diisocyanate and/or hexane diisocyanate as diisocyanate components and butanediol, hexanediol and/or polyalkylene glycols as diol components with molecular 30 weights of from 200 to 30 000.

Examples of suitable stabilizers and UV absorbers which may be metered into the continuous kneader during the direct synthesis process are piperidine derivatives, 35 benzophenone derivatives, benzotriazole derivatives, triazine derivatives and/or benzofuranone derivatives.

Examples of suitable auxiliaries which may be metered into the continuous kneader during the direct synthesis

process are latent hardeners, such as ammonium sulphate and/or ammonium chloride, and/or processing aids such as calcium stearate, magnesium stearate and/or waxes.

5 The particular advantage of the direct synthesis process of the invention is that the molecular weight of the etherified melamine resin condensates can be controlled with precision via the addition of C<sub>4</sub>-C<sub>18</sub> alcohols and/or diols represented by the type HO-R-OH. Without addition  
10 of C<sub>4</sub>-C<sub>18</sub> alcohols and/or diols represented by the type HO-R-OH, the increase in molecular weight in the etherified melamine resin condensates takes place in an uncontrolled manner by way of the azomethine groups present therein. The regulator function of the added C<sub>4</sub>-  
15 C<sub>18</sub> alcohols and/or diols represented by the type HO-R-OH consists in the deactivation, by their hydroxy groups, of the azomethine groups present in the etherified melamine resin condensates. When diols are added, the deactivation takes place with simultaneous linking of  
20 two melamine resin clusters.

The inventively prepared etherified melamine resin condensates have average molecular weights of from 500 to 50 000.

25 The inventively prepared etherified melamine resin condensates are preferably mixtures with average molecular weights of from 500 to 2 500, particularly preferably from 800 to 1 500, composed of tris(methoxy-methylamino)triazine and its higher-molecular-weight  
30 oligomers.

The etherified melamine resin condensates prepared by the process of the invention are preferably suitable for  
35 processing in the melt, in particular as hot-melt adhesives and for producing sheets, pipes, profiles, injection mouldings, fibres, coatings and foams, or for processing from solution or dispersion in the form of an adhesive, impregnating resin, surface-coating resin or

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laminating resin or for producing foams, microcapsules  
or fibres.

The particular advantage of the etherified melamine resin condensates prepared by the direct synthesis process with average molecular weights of from 500 to 50 000 is that, due to higher melt viscosity when  
5 compared with conventional triazine derivative precondensates, such as melamine-formaldehyde precondensates, they can be processed like thermoplastics by processes operating in the melt, and that the hardness and flexibility of the resultant  
10 products are adjustable over a wide range of properties.

When comparison is made with moulding compositions based on low-molecular-weight amino plastic precondensates, there is a dramatic reduction in the proportion of  
15 volatile cleavage products present during the curing of the etherified melamine resin condensates prepared by the direct synthesis process, during the shaping of the melt to give the product. For this reason, crack-free products can be produced from the etherified melamine  
20 resin condensates with short cycle times.

Preferred application sectors for the etherified melamine resin condensates prepared by the direct synthesis process are hot-melt adhesives, and also the  
25 production of sheets, pipes, profiles, injection mouldings, fibres and foams.

As long as they do not comprise any fillers or any other reactive polymers, the etherified melamine resin  
30 condensates prepared by the direct synthesis process are soluble in polar solvents of the type represented by C<sub>1</sub>-C<sub>10</sub> alcohols, dimethylformamide or dimethyl sulphoxide in concentrations of up to 60% by weight. The solutions or dispersions are suitable as an adhesive, impregnating  
35 agent, surface-coating resin formulation or laminating resin formulation, or for producing foams, microcapsules or fibres. The advantages of the solutions or dispersions of the etherified melamine resin condensates prepared by the direct synthesis process, when compared

with conventional triazine resin precondensates are higher viscosity and the resultant better flow properties or higher strengths of uncured intermediate products during the production of fibres or of foam.

5

The object is also achieved by way of melamine resin products which can be produced using the etherified melamine resin condensates prepared by the direct synthesis process.

10

The invention is illustrated by the following examples.

Inventive Example 1

15 A melamine dispersion is prepared by introducing 12.0 kg of melamine into 42.6 kg of methanol at 95°C in a stirred autoclave, and once a pH of 6 has been established in the stirred autoclave a mixture, temperature-controlled in advance to 90°C, of 10 kg of  
20 formaldehyde, 2.7 kg of methanol and 16.6 kg of water is metered in under pressure as formaldehyde component, and the reaction mixture is reacted at a reaction temperature of 95°C for a reaction time of 5 min.

25 After cooling to 65°C, a pH of 9 is established by adding N/10 sodium hydroxide solution, and the etherified melamine resin precondensate dissolved in the water/methanol mixture is transferred, after addition of 21.0 kg of butanol, into a first vacuum  
30 evaporator, in which the solution of the etherified melamine resin precondensate is concentrated at 80°C to give a highly concentrated melamine resin solution whose solids content is 75% by weight.

and whose butanol content is 10% by weight.

The highly concentrated solution of the etherified melamine resin is subsequently transferred into a  
5 second vacuum evaporator and concentrated at 90°C to give a syrupy melt whose solids content is 95% by weight and whose butanol content is 5% by weight.

The syrupy melt is metered into the feed hopper of a  
10 GL 27 D44 (Leistritz) laboratory extruder with vacuum venting downstream of the reaction zone prior to product discharge, temperature profile 220°C/220°C/220°C/240°C/240°C/240°C/240°C/240°C/190°C/150°C, extruder rotation rate 150 rpm, and, after a residence  
15 time of 3.2 min in the reaction zone, volatile content is removed at 100 mbar, and the discharged extrudate is chopped in a pelletizer.

The etherified melamine resin condensate has a weight-average molecular weight (GPC) of 800 and a butoxy group content of 4.1% by weight. Neither hydroxymethyleneamino groups bonded to the triazine rings of the melamine resin condensate nor -NH-CH<sub>2</sub>-O-CH<sub>2</sub>-NH- groups linking triazine rings are discernible  
25 in the IR spectrum.

#### Inventive Example 2

A melamine dispersion is prepared by introducing  
30 12.0 kg of melamine into 42.6 kg of methanol at 95°C in a stirred autoclave, and once a pH of 6.1 has been established in the stirred autoclave a mixture, temperature-controlled in advance to 92°C, of 8.6 kg of formaldehyde and 8.6 kg of water is metered in under  
35 pressure as formaldehyde component, and the reaction mixture is reacted at a reaction temperature of 95°C

for a reaction time of 6 min. After cooling to 65°C, a pH of 9.2 is established by adding N/10 sodium hydroxide solution, and the etherified melamine resin precondensate dissolved in the water/methanol mixture is transferred into a first vacuum evaporator, in which the solution of the etherified melamine resin precondensate is concentrated at 80°C to give a highly concentrated melamine resin solution whose solids content is 78% by weight.

10

The highly concentrated solution of the etherified melamine resin is subsequently mixed, in a mixing section, with 0.8 kg of Simulsol BPLE (oligoethylene glycol ether of bisphenol A), transferred into a second vacuum evaporator and concentrated at 90°C to give a syrupy melt whose solids content is 98% by weight and whose butanol content is 2% by weight.

15

The syrupy melt is metered into the feed hopper of a GL 27 D44 (Leistritz) laboratory extruder with vacuum venting zones downstream of the feed zone and also downstream of the reaction zone prior to product discharge, temperature profile 220°C/220°C/220°C/240°C/240°C/240°C/240°C/240°C/190°C/150°C, extruder rotation rate 150 rpm, and the reaction mixture is devolatilized at 150 mbar, and, after a residence time of 3.2 min in the reaction zone, volatile content is removed at 100 mbar, and the discharged extrudate is chopped in a pelletizer.

25

30

The etherified melamine resin condensate has a weight-average molecular weight (GPC) of 10 000. Neither hydroxymethyleneamino groups bonded to the triazine rings of the melamine resin condensate nor -NH-CH<sub>2</sub>-O-CH<sub>2</sub>-NH- groups linking triazine rings are discernible in the IR spectrum.

35

Inventive Example 3

A melamine dispersion is prepared by introducing 12.0 kg of melamine into 42.6 kg of methanol at 95°C in a stirred autoclave, and once a pH of 5.9 has been established in the stirred autoclave a mixture, temperature-controlled in advance to 90°C, of 8.6 kg of formaldehyde, 3.5 kg of methanol and 9.9 kg of water is metered in under pressure as formaldehyde component, and the reaction mixture is reacted at a reaction temperature of 95°C for a reaction time of 10 min.

After cooling to 65°C, a pH of 9 is established by adding N/10 sodium hydroxide solution, and the etherified melamine resin precondensate dissolved in the water/methanol mixture is transferred, after addition of 21.0 kg of butanol, into a first vacuum evaporator, in which the solution of the etherified melamine resin precondensate is concentrated at 82°C to give a highly concentrated melamine resin solution whose solids content is 76% by weight and whose butanol content is 8% by weight.

The highly concentrated solution of the etherified melamine resin is subsequently transferred into a second vacuum evaporator and concentrated at 90°C to give a syrupy melt whose solids content is 96% by weight and whose butanol content is 4.5% by weight.

The syrupy melt, mixed in a mixing section with 5.0 kg of polyethylene glycol (molecular weight 800), is metered into the feed hopper of a GL 27 D44 laboratory extruder with vacuum venting zones downstream of the feed zone and downstream of the reaction zone prior to product discharge, temperature profile 220°C/220°C/220°C/240°C/240°C/240°C/240°C/240°C/240°C/190°C/150°C, extruder rotation rate 150 rpm, and the



reaction mixture is devolatilized at 150 mbar, and, after a residence time of 3.1 min in the reaction zone, volatile content is removed at 100 mbar, and the discharged extrudate is chopped in a pelletizer.

5

The etherified melamine resin condensate has a weight-average molecular weight (GPC) of 20 000 and a butoxy group content below 0.5% by weight. Neither hydroxymethyleneamino groups bonded to the triazine  
10 rings of the melamine resin condensate nor -NH-CH<sub>2</sub>-O-CH<sub>2</sub>-NH- groups linking triazine rings are discernible in the IR spectrum.

#### Inventive Example 4

15

A melamine dispersion is prepared by introducing 1.0 kg of melamine into 3.6 kg of methanol at 98°C in a 10 l stirred autoclave, and once a pH of 6 has been established in the stirred autoclave 0.84 kg of p-  
20 formaldehyde is metered in as formaldehyde component, and stirring of the reaction mixture is continued at a reaction temperature of 95°C until a clear solution has been obtained at that temperature.

25

After cooling to 65°C, a pH of 9 is established by adding N/10 sodium hydroxide solution, and the dissolved etherified melamine resin precondensate is transferred, after addition of 2.0 kg of butanol, into a first vacuum evaporator, in which the solution of the  
30 etherified melamine resin precondensate is concentrated at 80°C to give a highly concentrated melamine resin solution whose solids content is 79% by weight and whose butanol content is 7% by weight.

The highly concentrated solution of the etherified melamine resin is subsequently transferred into a second vacuum evaporator and concentrated at 90°C to give a syrupy melt whose solids content is 96% by weight and whose butanol content is 3.4% by weight.

The syrupy melt is metered into the feed hopper of a GL 27 D44 (Leistritz) laboratory extruder with vacuum venting downstream of the reaction zone prior to product discharge, temperature profile 220°C/220°C/220°C/240°C/240°C/240°C/240°C/240°C/190°C/150°C, extruder rotation rate 150 rpm, and, after a residence time of 3.2 min in the reaction zone, volatile content is removed at 100 mbar, and the discharged extrudate is chopped in a pelletizer.

The etherified melamine resin condensate has a weight-average molecular weight (GPC) of 4 200 and a butoxy group content of 3.8% by weight. Neither hydroxymethyleneamino groups bonded to the triazine rings of the melamine resin condensate nor -NH-CH<sub>2</sub>-O-CH<sub>2</sub>-NH- groups linking triazine rings are discernible in the IR spectrum.

#### Inventive Example 5

A melamine dispersion is prepared by introducing 12.0 kg of melamine into 42.6 kg of methanol at 99°C in a 100 l stirred autoclave, and once a pH of 6.1 has been established in the stirred autoclave a mixture, temperature-controlled in advance to 92°C, of 8.6 kg of formaldehyde and 8.6 kg of water is metered in under pressure as formaldehyde component, and the reaction mixture is reacted at a reaction temperature of 90°C for a reaction time of 15 min.

After cooling to 65°C, a pH of 9.0 is established by adding N/10 sodium hydroxide solution, and the etherified melamine resin precondensate dissolved in the water/methanol mixture is transferred, after  
5 addition of 10 kg of butanol, into a first vacuum evaporator, in which the solution of the etherified melamine resin precondensate is concentrated at 80°C to give a highly concentrated melamine resin solution whose solids content is 80% by weight and whose butanol  
10 content is 3.4% by weight.

The highly concentrated solution of the etherified melamine resin is subsequently mixed in a mixing section with 2.0 kg of bis(hydroxyethyl)terephthalate  
15 and transferred into a second vacuum evaporator and concentrated at 90°C to give a syrupy melt whose solids content is 98.5% by weight and whose butanol content is 1.5% by weight.

20 The syrupy melt is metered into the feed hopper of a GL 27 D44 (Leistritz) laboratory extruder with vacuum venting zones downstream of the feed zone and downstream of the reaction zone upstream of the ancillary-stream metering equipment, temperature  
25 profile 220°C/220°C/220°C/240°C/240°C/240°C/240°C/240°C/240°C/190°C/150°C, extruder rotation rate 150 rpm, and the reaction mixture is devolatilized at 150 mbar, and, after a residence time of 3.2 min in the reaction zone, volatile content is removed at 100 mbar, 4% by  
30 weight of Na montmorillonite (Südchemie AG) and 6% by weight of polyamide D1466 (Ems-Chemie), in each case based on the melamine used, being metered into the

melt by way of the ancillary-flow metering equipment and homogenized and the discharged extrudate is chopped in a pelletizer.

5 Inventive Example 6

10 The modified filled melamine resin ether of inventive Example 5 is finely ground to an average particle diameter of 0.07 mm, and used to produce preregs via powdered application to cellulose nonwovens (120 g/m<sup>2</sup> Lenzing AG, Austria) followed by melting of the powder at about 160°C in a field of infrared radiation. The amount of resin applied to the cellulose nonwoven preregs produced is about 45% by weight.

15

The preregs are cut to a size of 30 × 20 cm. To produce a moulding with curved edges similar to a U profile, three preregs and an untreated cellulose nonwoven forming an upper side are mutually superposed in a compression mould (30 × 20 cm) preheated to 160°C, and the press is slowly closed, the preregs being capable of slight deformation during this process since the resin has not yet cured. The temperature is raised to 185°C under a pressure of 150 bar and the material is compression moulded for 12 min. The finished workpiece is removed and slowly cooled, and the flash produced by resin discharged at the vertical flash face of the compression mould is removed by grinding.

30 In the flexural test, specimens cut by a rotary cutter from the workpiece have a modulus of elasticity of 5.8 GPa, an elongation at maximum force of 3.1% and an impact strength of 11.8 kJ/m<sup>2</sup>.

Even though the first stage of the process in the examples took place batchwise, the process of the invention may also be operated in a continuous system, using a reactor whose operation is correspondingly  
5 continuous.

The evaporators used may comprise falling-film evaporators, rotary evaporators, or else other types of evaporator.

10

The working of the invention is not restricted to the preferred examples given above. Rather, it is possible to conceive a number of variants which utilize fundamentally different embodiments of the inventive  
15 direct synthesis process, of the use of melamine resin products, and of the melamine resin products.

Patent claims

1. Direct synthesis process for preparing etherified melamine resin condensates with average molecular weights of from 500 to 50 000, wherein the melamine resin condensates are free from hydroxymethyleneamino groups bonded to the triazine rings of the melamine resin condensate and from  $\text{-NH-CH}_2\text{-O-CH}_2\text{-NH-}$  groups which link triazine rings,  
characterized in that
  - a) in the first step of the reaction, an etherified melamine resin precondensate is prepared in alcoholic solution,
  - b) in at least one vaporization step, the concentration of the etherified melamine resin precondensate in alcoholic solution is increased,  $\text{C}_4\text{-C}_{18}$  alcohols, diols of the type represented by  $\text{HO-R-OH}$  and/or tetrahydric alcohols based on erythritol being added to the melamine resin precondensate prior to, during and/or after the concentration-increase process,
  - c) in a second step of the reaction, the increased-concentration melamine resin precondensate is reacted, using a mixer, in particular a kneader.
2. Direct synthesis process according to Claim 1, characterized in that, after the second step of the reaction, the etherified melamine resin condensate is discharged and pelletized.
3. Direct synthesis process according to Claim 1 or 2, characterized in that the alcohol in the first step of the reaction is methanol.
4. Direct synthesis process according to at least one of the preceding claims, characterized in that, in

the first step of the reaction, the methylation of the melamine takes place with subsequent etherification.

5 5. Direct synthesis process according to at least one of the preceding claims, characterized in that, in the first step of the process, formaldehyde is used in the form of formalin solution at variable concentration and/or paraformaldehyde.

10

5. Direct synthesis process according to Claim 4, characterized in that the methylation takes place at a pH of from 7 to 9 and the etherification takes place at a pH of from 5.5 to 6.5.

15

6. Direct synthesis process according to at least one of Claims 1 to 4, characterized in that, in the first step of the reaction, the methylation and the etherification take place simultaneously.

20

7. Direct synthesis process according to Claim 6, characterized in that the first step of the reaction takes place at a pH of from 5.5 to 6.5.

25

8. Direct synthesis process according to at least one of the preceding claims, characterized in that the first step of the reaction takes place in the presence of acidic, or of a mixture of acidic and basic, ion exchangers.

30

9. Direct synthesis process according to at least one of the preceding claims, characterized in that, in the first step of the reaction, a reaction temperature of from 70 to 160°C, in particular from 95 to 100°C, is established.

35

10. Direct synthesis process according to at least one of the preceding claims, characterized in that the

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first step of the reaction is carried out using a  
melamine/formaldehyde molar ratio



of from 1 : 2.0 to 1 : 4.0.

11. Direct synthesis process according to at least one  
of the preceding claims, characterized in that the  
5 increased-concentration melamine resin precondensate  
obtained after the vaporization process has a  
concentration of from 95 to 99% by weight.

12. Direct synthesis process according to at least one  
10 of the preceding claims, characterized in that the  
vaporization of the low-molecular-weight components  
takes place in two stages.

13. Direct synthesis process according to at least one  
15 of the preceding claims, characterized in that use is  
made of at least one diol represented by the type HO-R-  
OH with molecular weight of from 62 to 20 000 or of a  
mixture of at least two diols represented by the type  
HO-R-OH with molecular weights of from 62 to 20 000,  
20 where the substituent R may have one of the following  
structures

C<sub>2</sub>-C<sub>18</sub>-alkylene,

-CH(CH<sub>3</sub>)-CH<sub>2</sub>-O-(C<sub>2</sub>-C<sub>12</sub>)-alkylene-O-CH<sub>2</sub>-CH(CH<sub>3</sub>)-,

-CH(CH<sub>3</sub>)-CH<sub>2</sub>-O-(C<sub>2</sub>-C<sub>12</sub>)-arylene-O-CH<sub>2</sub>-CH(CH<sub>3</sub>)-,

25 - (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-)<sub>x</sub>-(CH<sub>2</sub>-CHR)<sub>y</sub>-

-[CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>]<sub>n</sub>-,

-[CH<sub>2</sub>-CH(CH<sub>3</sub>)-O-CH<sub>2</sub>-CH(CH<sub>3</sub>)]<sub>n</sub>-,

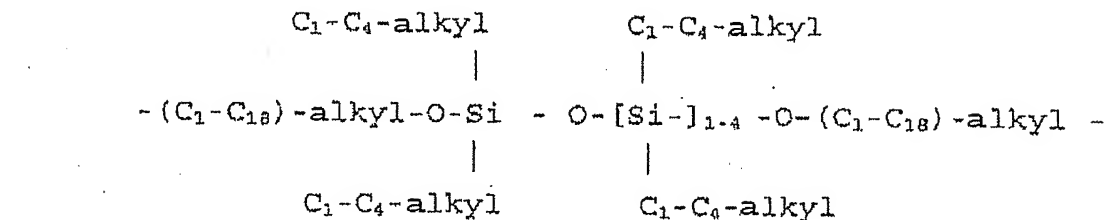
-[-O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-]<sub>n</sub>-,

-[(CH<sub>2</sub>)<sub>2-8</sub>-O-CO-(C<sub>6</sub>-C<sub>14</sub>)-arylene-CO-O-(CH<sub>2</sub>)<sub>2-8</sub>]<sub>n</sub>-,

30 -[(CH<sub>2</sub>)<sub>2-8</sub>-O-CO-(C<sub>2</sub>-C<sub>12</sub>)-alkylene-CO-O-(CH<sub>2</sub>)<sub>2-8</sub>]<sub>n</sub>-,

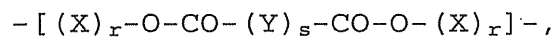
where n = 1 - 200; x = 5 - 15;

sequences which contain siloxane groups and are represented by the type

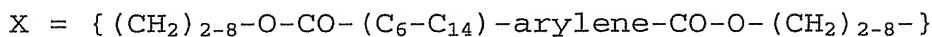


5

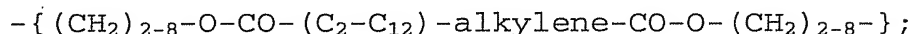
polyester sequences which contain siloxane groups and are represented by the type



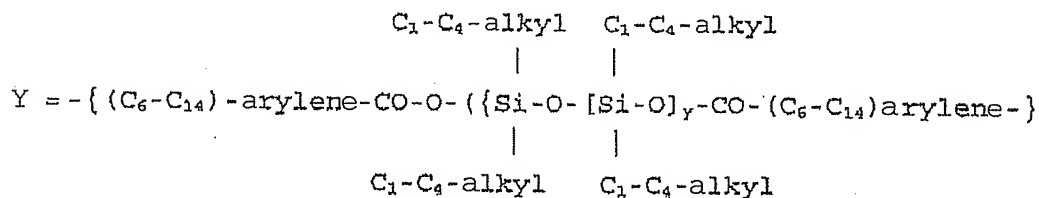
10 where



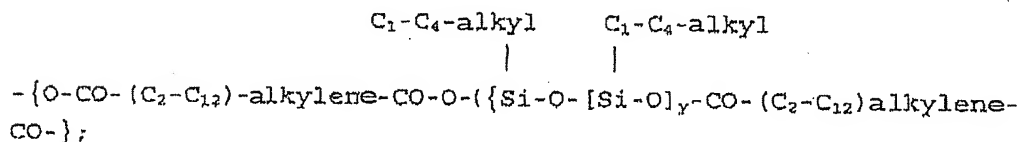
or



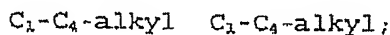
15



or

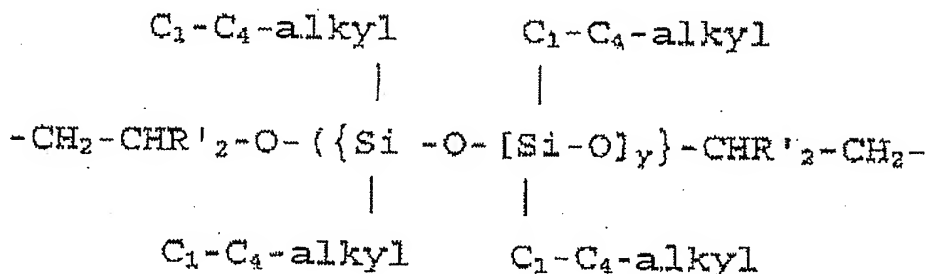


20



where  $r = 1 - 70$ ;  $s = 1 - 70$  and  $y = 3 - 50$ ;

polyether sequences which contain siloxane groups and are represented by the type



5 where  $R'_2 = H$ ;  $C_1\text{-C}_4\text{-alkyl}$  and  $y = 3 - 50$ ;

sequences based on alkylene oxide adducts of melamine and represented by the type of

10 2-amino-4,6-di-( $C_2\text{-C}_4$ )alkyleneamino-1,3,5-triazine sequences

phenol ether sequences based on dihydric phenols and on  $C_2\text{-C}_8$  diols and represented by the type of

15  $\text{-(C}_2\text{-C}_8\text{)alkylene-O-(C}_6\text{-C}_{18}\text{)-arylene-O-(C}_2\text{-C}_8\text{)-}$  alkylene sequences.

14. Direct synthesis process according to at least one of the preceding claims, characterized in that the etherified melamine resin condensates are mixtures with  
20 average molecular weights of from 500 to 2500 composed of tris(methoxymethylamino)triazine and its higher-molecular-weight oligomers.

15. Direct synthesis process according to at least one  
25 of the preceding claims, characterized in that, prior to and/or during the concentration-increase process, i.e. prior to the first and/or prior to the second vaporizing stage and/or after the concentration-increase process, i.e. prior to the second step of the  
30 reaction, anhydrides and/or acids dissolved in alcohols or in water are added to the melamine resin precondensate.

16. Direct synthesis process according to at least one of the preceding claims, characterized in that the kneader is a continuously operating, at least to some extent self-cleaning, extruder with vacuum venting.

5

17. Direct synthesis process according to at least one of the preceding claims, characterized in that the kneader used comprises a twin-screw extruder with vent zones.

10

18. Direct synthesis process according to at least one of the preceding claims, characterized in that, in the continuous kneader, up to 75% by weight of fillers and/or reinforcing fibres, other reactive polymers of the type represented by ethylene copolymers, maleic anhydride copolymers, modified maleic anhydride copolymers, poly(meth)acrylates, polyamides, polyesters and/or polyurethanes are also incorporated, as are up to 2% by weight of stabilizers, UV absorbers and/or auxiliaries, each weight being based on the etherified melamine resin condensates.

15

20

19. Direct synthesis process according to at least one of the preceding claims, characterized in that the first step of the reaction is executed in a stirred tank or in a continuous reactor.

25

20. Direct synthesis process according to at least one of the preceding claims, characterized in that the process is carried out either continuously or batchwise.

30

21. Use of etherified melamine resin condensates prepared by a direct synthesis process according to at least one of claims 1 to 20 for processing in the melt, in particular in the form of hot-melt adhesives and for producing sheets, pipes, profiles, injection mouldings, fibres, coatings and foams, or for processing from solution or dispersion in the form of an adhesive,

35

impregnating resin, surface-coating resin or laminating resin or for producing foams, microcapsules or fibres.

22. Melamine resin products, produced via a melamine  
5 resin condensate etherified using a direct synthesis  
process according to at least one of Claims 1 to 20.

# Abstract

Direct synthesis process for preparing etherified  
melamine resin condensates, melamine resin condensates  
5 and their use

The invention relates to a direct synthesis process for  
preparing etherified melamine resin condensates with  
average molecular weights of from 500 to 50 000,  
10 wherein the melamine resin condensates are free from  
hydroxymethyleneamino groups bonded to the triazine  
rings of the melamine resin condensate and from -NH-  
CH<sub>2</sub>-O-CH<sub>2</sub>-NH- groups which link triazine rings,  
characterized in that

15 a) in the first step of the reaction, an etherified  
melamine resin precondensate is prepared in alcoholic  
solution,

20 b) in at least one vaporization step, the concentration  
of the etherified melamine resin precondensate in  
alcoholic solution is increased, C<sub>4</sub>-C<sub>18</sub> alcohols, diols  
of the type represented by HO-R-OH and/or tetrahydric  
alcohols based on erythritol being added to the  
25 melamine resin precondensate prior to, during and/or  
after the concentration-increase process,

c) in a second step of the reaction, the increased-  
concentration melamine resin precondensate is reacted,  
30 using a mixer, in particular a kneader. Melamine resin  
condensates with average molecular weights of from 500  
to 50 000 can be prepared in this way and are free from  
hydroxymethyleneamino groups bonded to the triazine  
rings and from -NH-CH<sub>2</sub>-O-CH<sub>2</sub>-NH- groups which link the  
35 triazine rings.